The Land Breeze and $ClNO_2$ production over Santa Monica Bay

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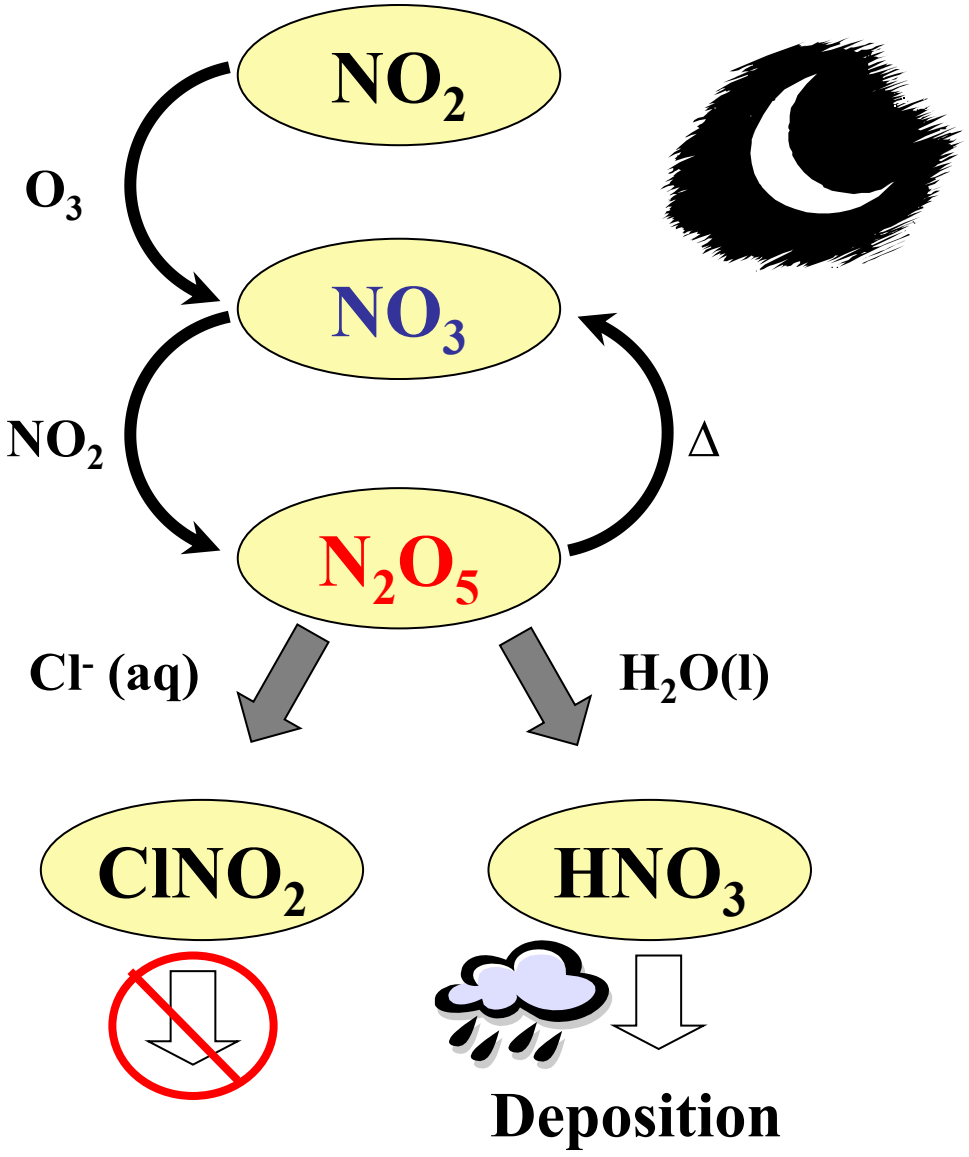
AtlantiCaLNex

Outline:

1) Sea breeze and land breeze in Santa Monica Bay.
2) $ClNO_2$ production in the land breeze.

$ClNO_2$ Production Mechanism

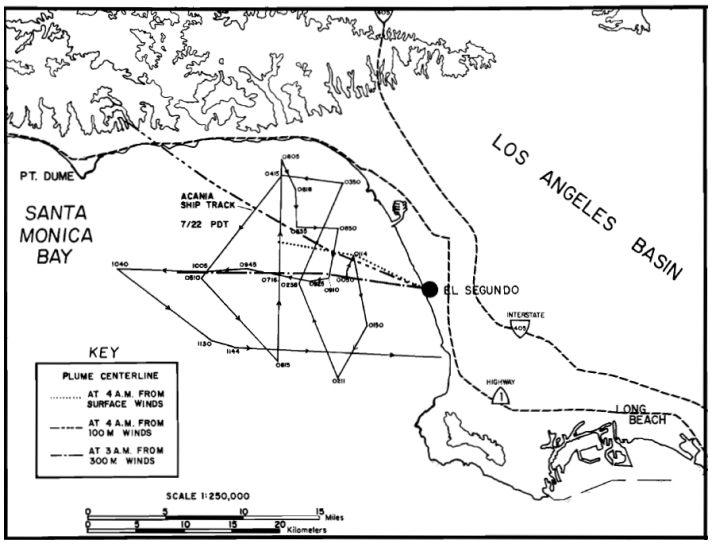
- O_3 and NO_2 react to produce NO_3. NO_3 is photoliable and exists in significant concentrations only at night.
- NO_3 and N_2O_5 are usually in chemical equilibrium and rapidly inter convert.
- NO_3 is lost to reactions with VOCs.
- N_2O_5 is lost to hydrolysis.
- Conventional view: In the aerosol N_2O_5 is converted into NO_3^- and HNO_3, which is lost to deposition.
- New mechanism: N_2O_5 is convert to $ClNO_2$ in aerosol with Cl^-. $ClNO_2$ builds throughout the night and is lost to photolysis in the morning.



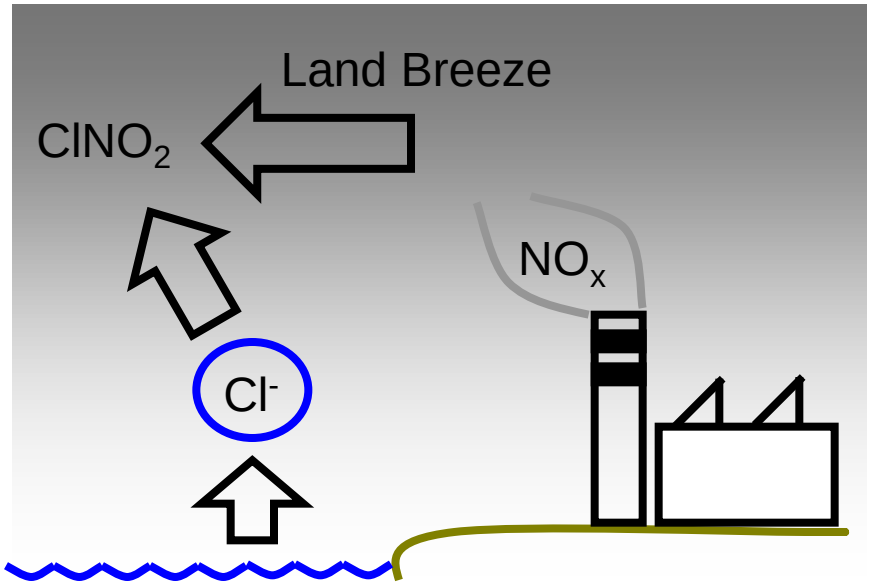
Cass and Shair Experiment – Observation of the Land Breeze

- 1970's transport study: SF_6 injected into power plant at El Segundo in early evening.
- Inferred transport in land breeze initiated aloft, eventually mixing to surface level.
- Return transport during sea breeze the following day.
- Pre-CalNex view of $ClNO_2$ production:

  $ClNO_2$ is produced in urban outflow over the ocean. The most consistent outflow is the land breeze over Santa Monica Bay.

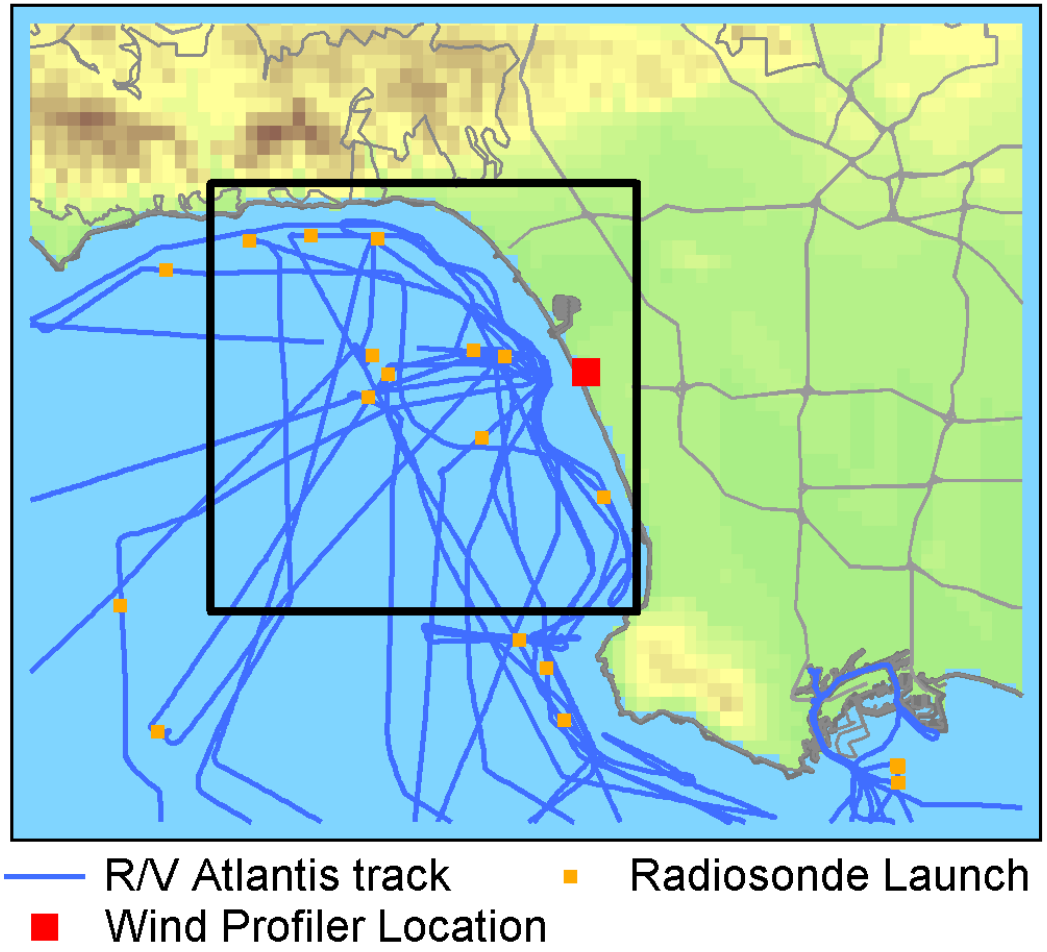


F. Shair, Atmos. Environ., 1982



CalNex Platforms

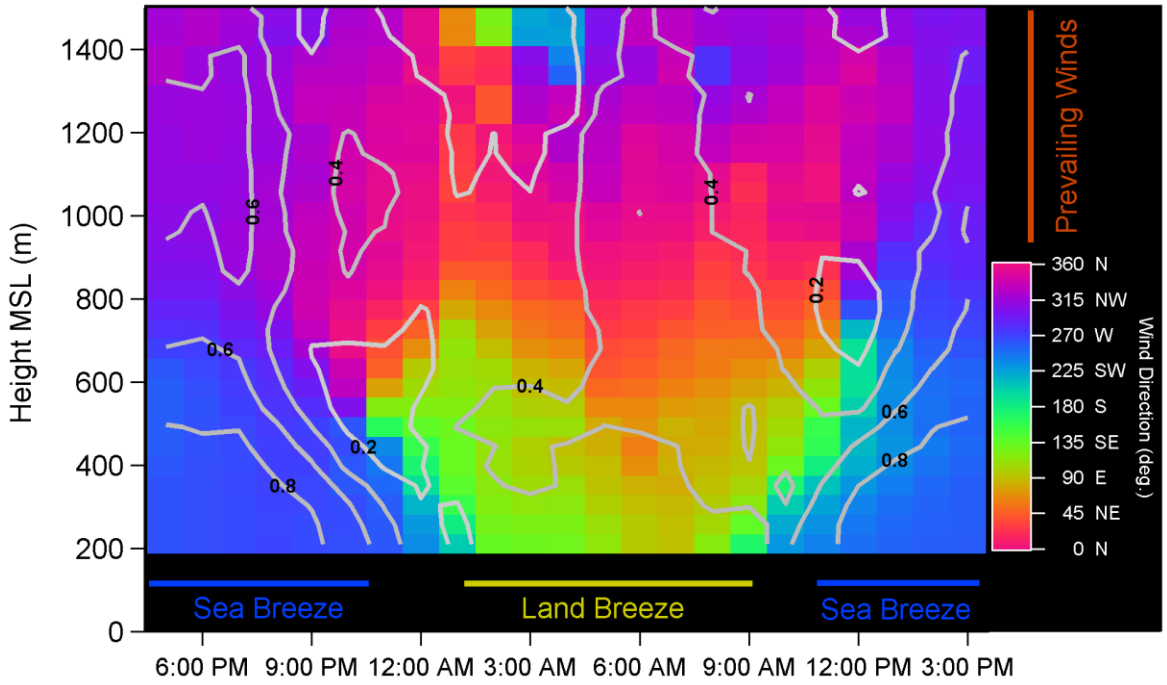
Santa Monica Bay

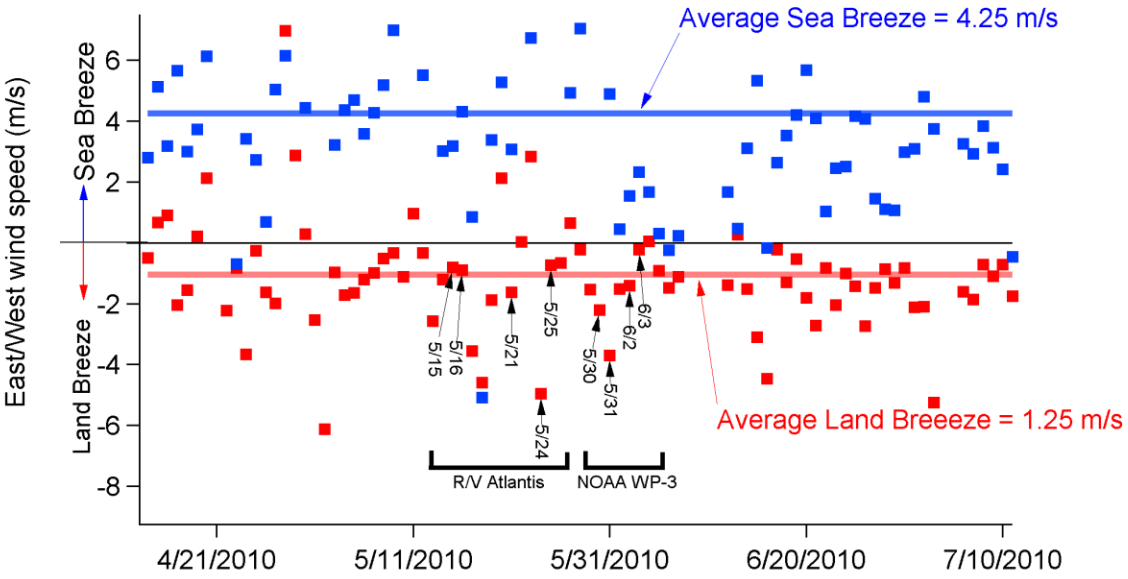


- Use measurements from R/V Atlantis in Santa Monica Bay, LAX wind profiler and P-3 vertical profiles over LAX.

LAX wind profiler

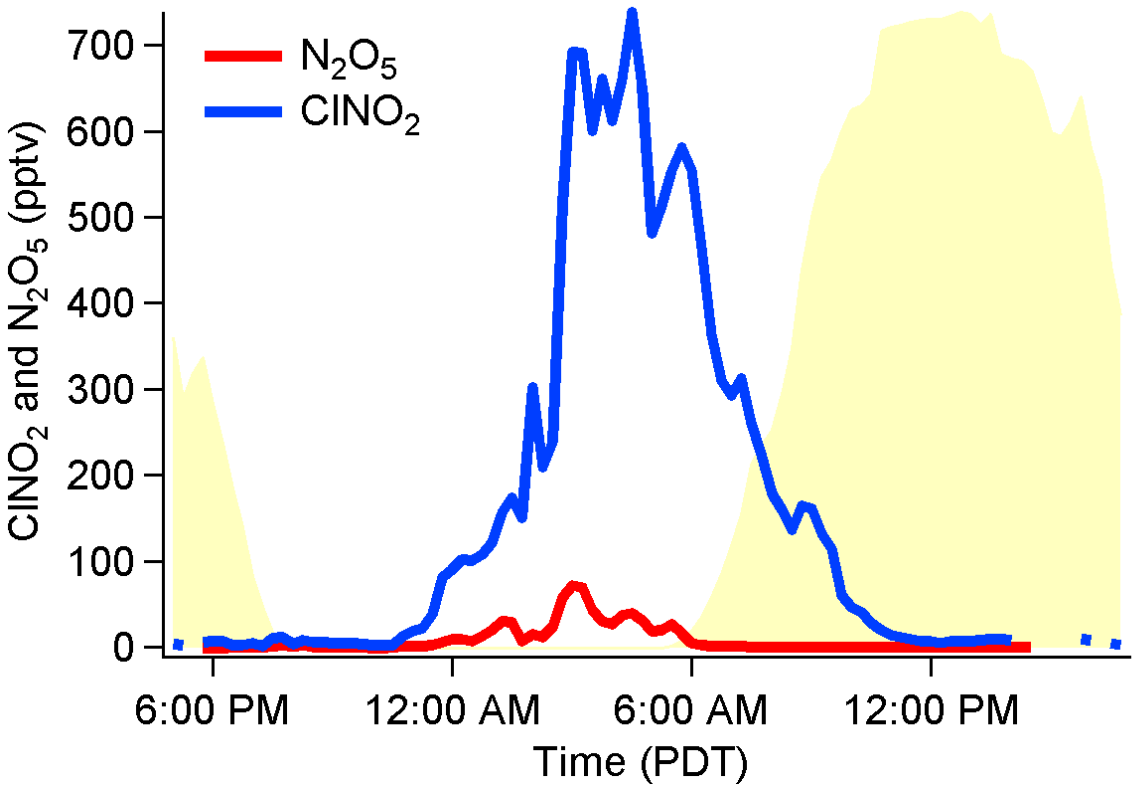
- Located on the coast of Santa Monica Bay.
- Data from mid-April through mid–July.
- Diurnally averaged wind direction shows a land breeze and sea breeze below 700 meters.
- The land breeze occurs on the majority of nights during spring.
- Observations from the R/V Atlantis and the NOAA P-3 were at times consistent with the entire period.





$ClNO_2$ Observed from the R/V Atlantis

- $ClNO_2$ is observed in the land breeze at mixing ratios as high as 2 ppbv.
- Use a box model to calculate $ClNO_2$ production over water and compare with measurements.

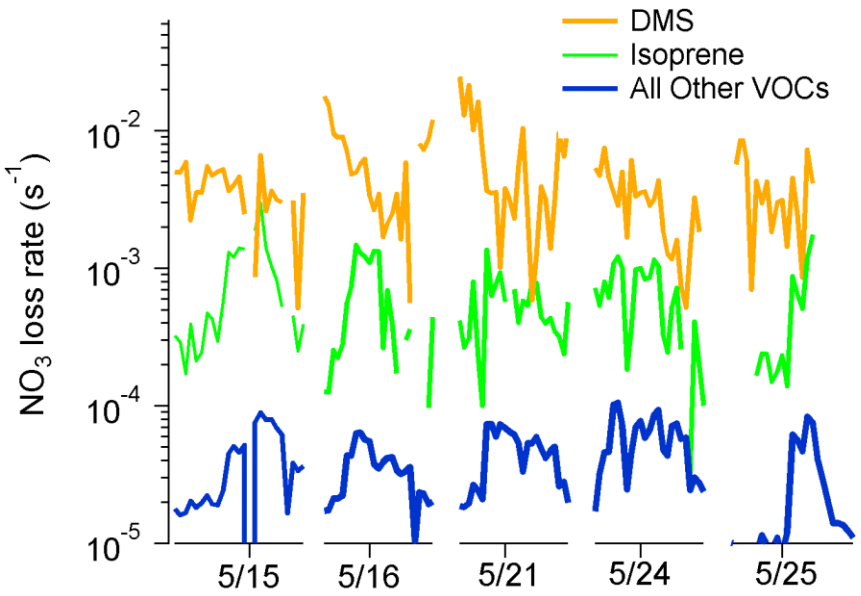


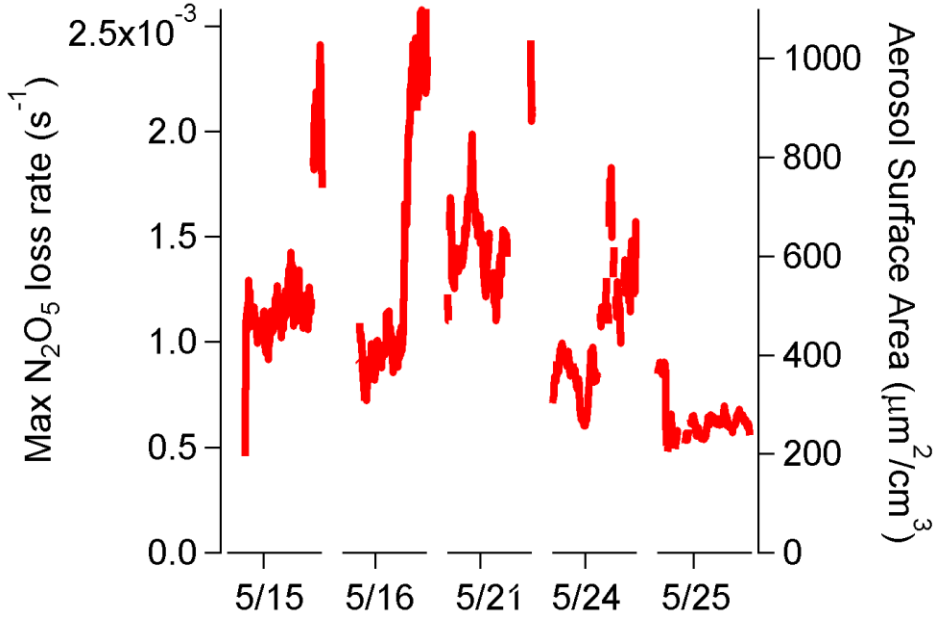
Box modeling of $ClNO_2$ production

- Reactions:

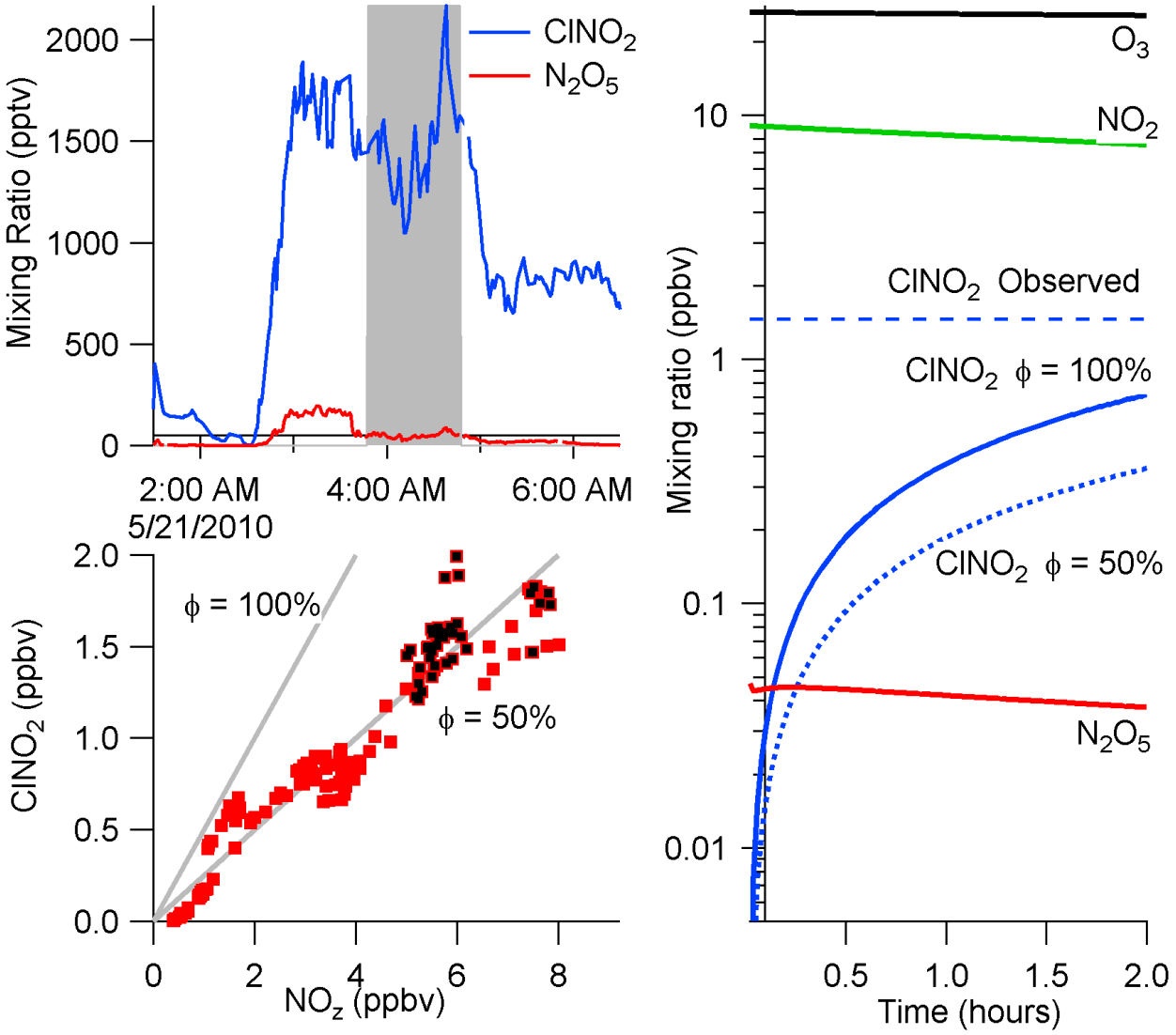
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \leftrightarrow N_2O_5$$
$$NO_3 + DMS \rightarrow products$$
$$N_2O_5 + H_2O(aq) \rightarrow 2HNO_3$$
$$N_2O_5 + Cl^-(aq) \rightarrow ClNO_2 + NO_3^-$$

- Wind speed and direction give the transport time from the coast.
- DMS concentration is used to estimate NO_3 loss rate.
- Upper limit for $ClNO_2$ production, because the maximum N_2O_5 uptake was assumed. (γ = 0.04)
- Used two different yields:
  ϕ =100% for upper limit
  ϕ = % of NO_z





Example Boxmodel Calculation

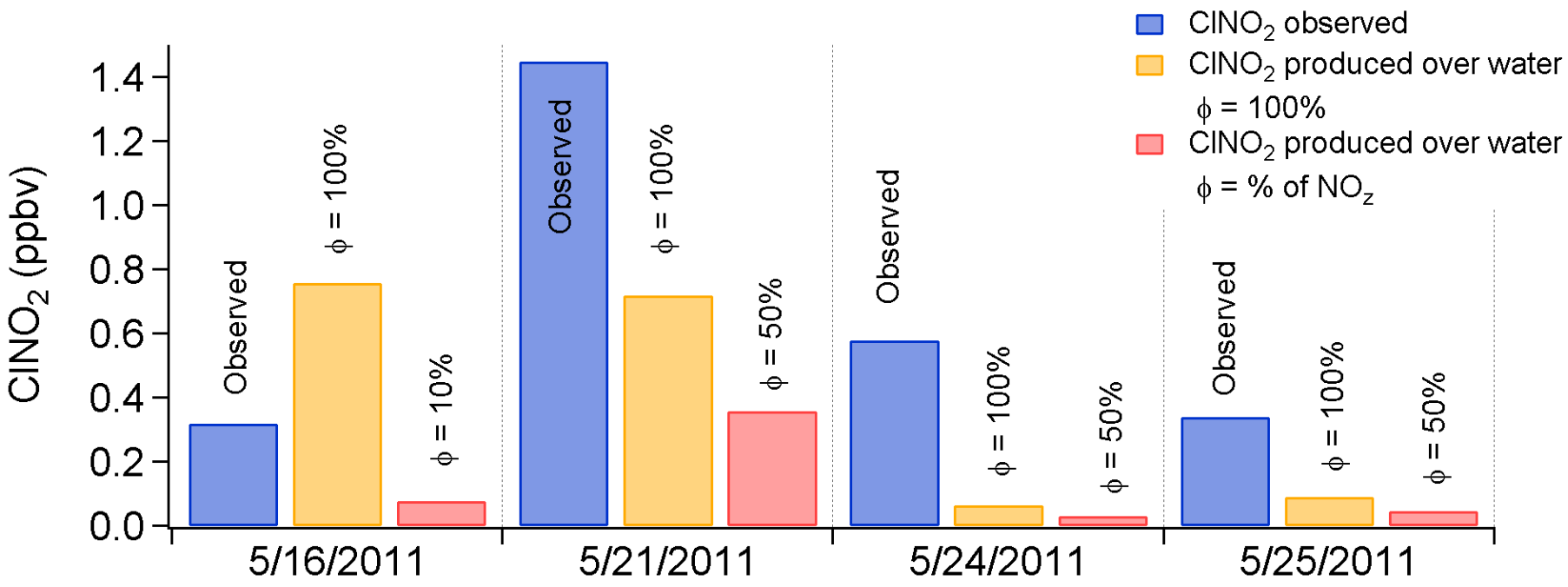


- Initialized the model to measured values of O_3, NO_2, and N_2O_5.

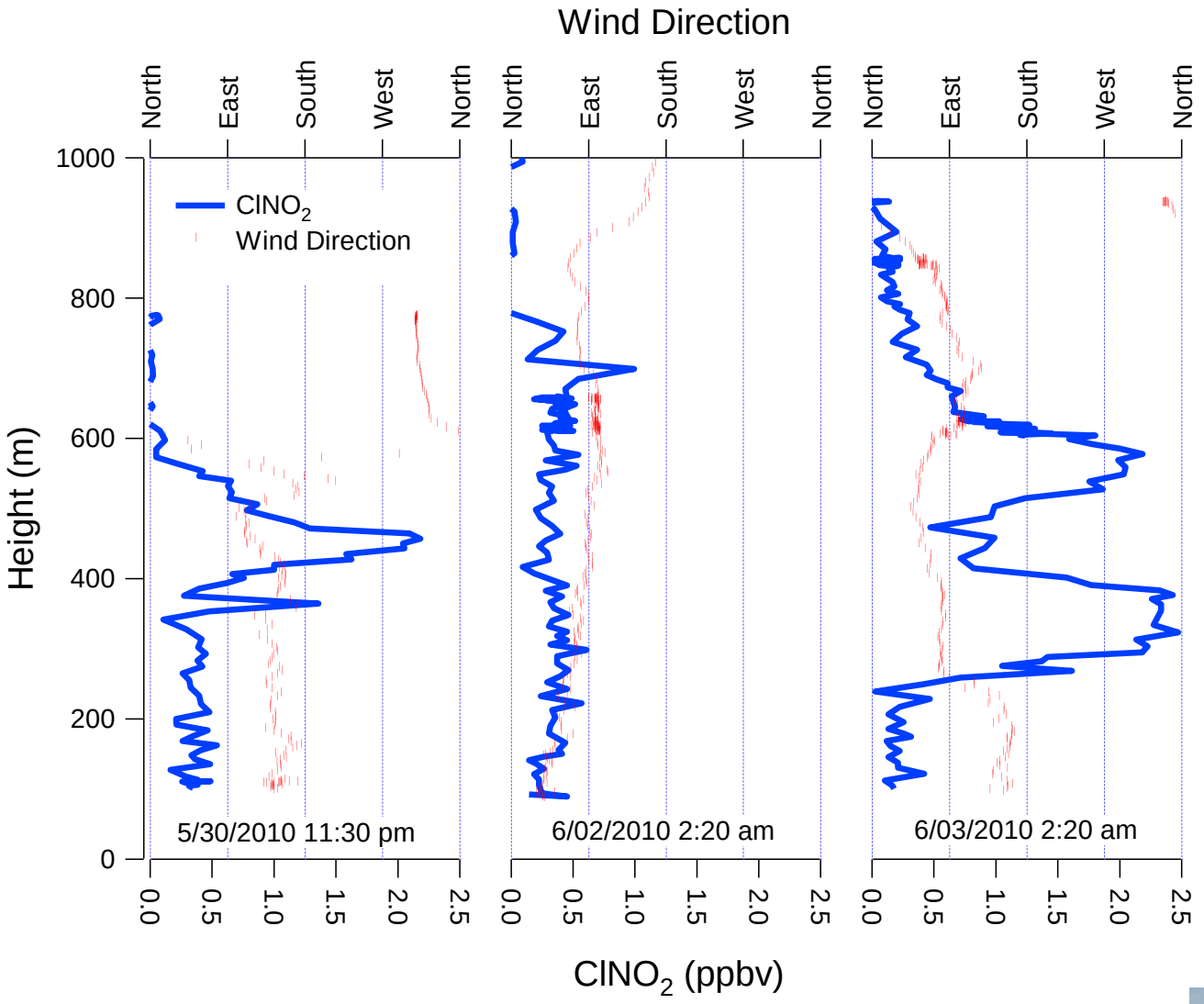
Results of Box Modeling

- Four nights in Santa Monica Bay during the land breeze were used.

•$ClNO_2$ production over water is insufficient to account for observed $ClNO_2$.



Aircraft Vertical Profiles over LAX – Transport of $ClNO_2$ into Santa Monica Bay

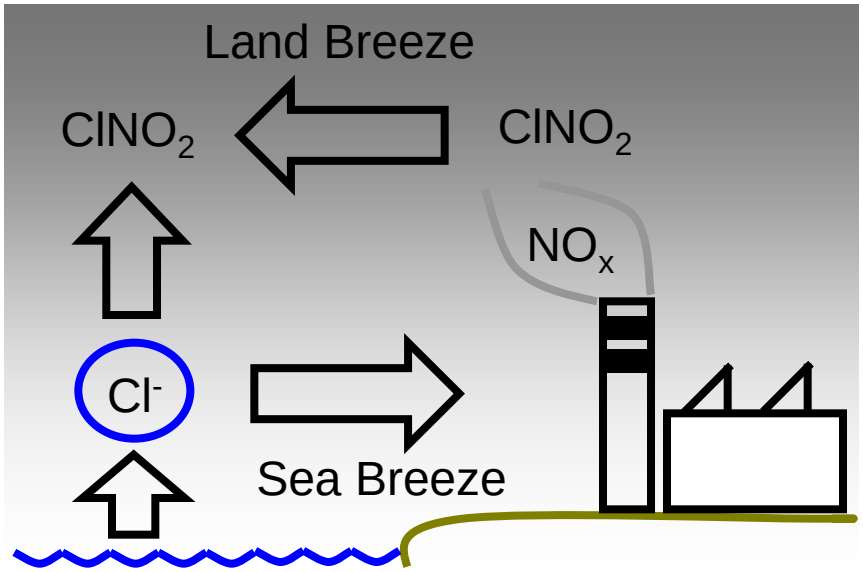


- Vertical profiles confirms transport of $ClNO_2$ into Santa Monica Bay.

Conclusions

Post-CalNex view:

$ClNO_2$ is produced over Santa Monica Bay. However, significant production occurs over land and some $ClNO_2$ is transported to Santa Monica Bay on the land breeze.

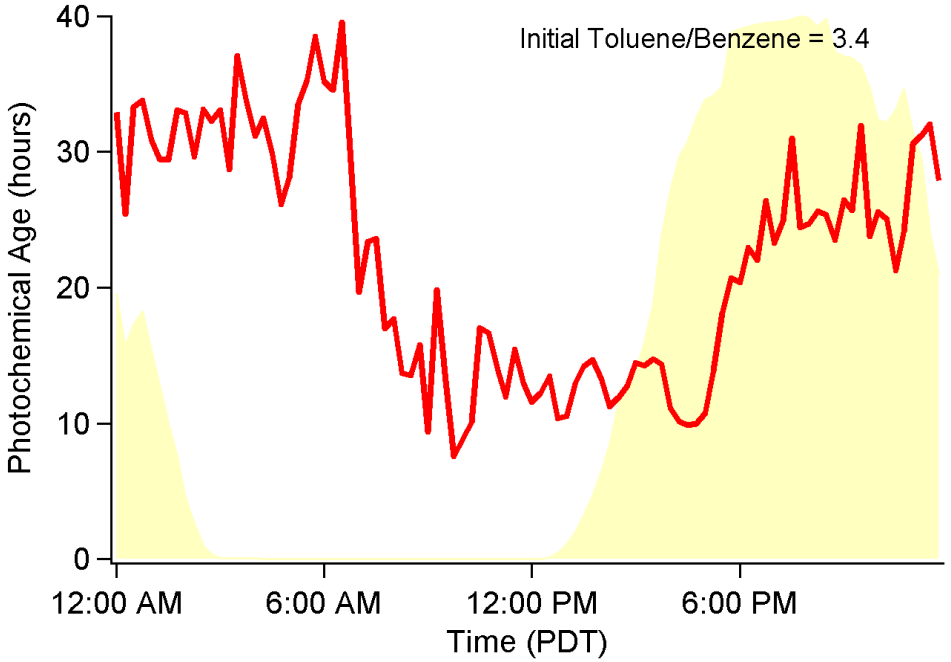


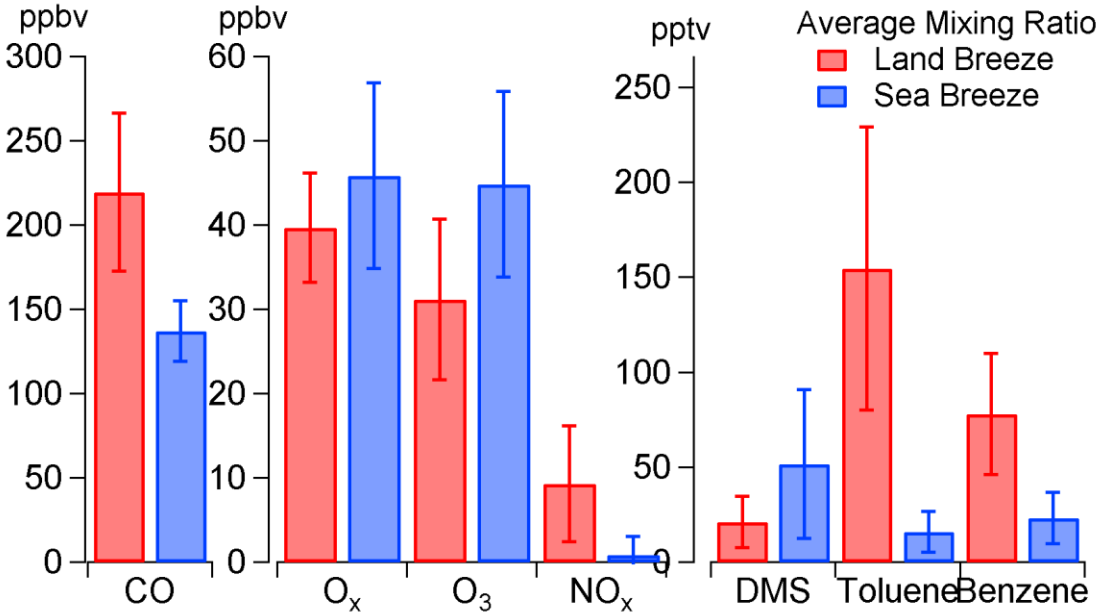
Production of $ClNO_2$ over land compared with over water.

- As the aerosol moves inland on the sea breeze it becomes more acidic. The acidification process allows Cl^- to move to particles with the most surface area. Gard, Science 279, 1184 (1998)
- High aerosol liquid water content over water dilutes Cl^- and reduces the yield. (future work?)
- Stronger sea breeze transports more Cl^- in land than NO_X is transported to sea in land breeze.
- See Levi Mielke's poster on $ClNO_2$ measurements at Pasadena ground site.

Composition of the Land Breeze

- In the land breeze are fresh urban emissions.
- The sea breeze is a more aged and dilute urban air mass.

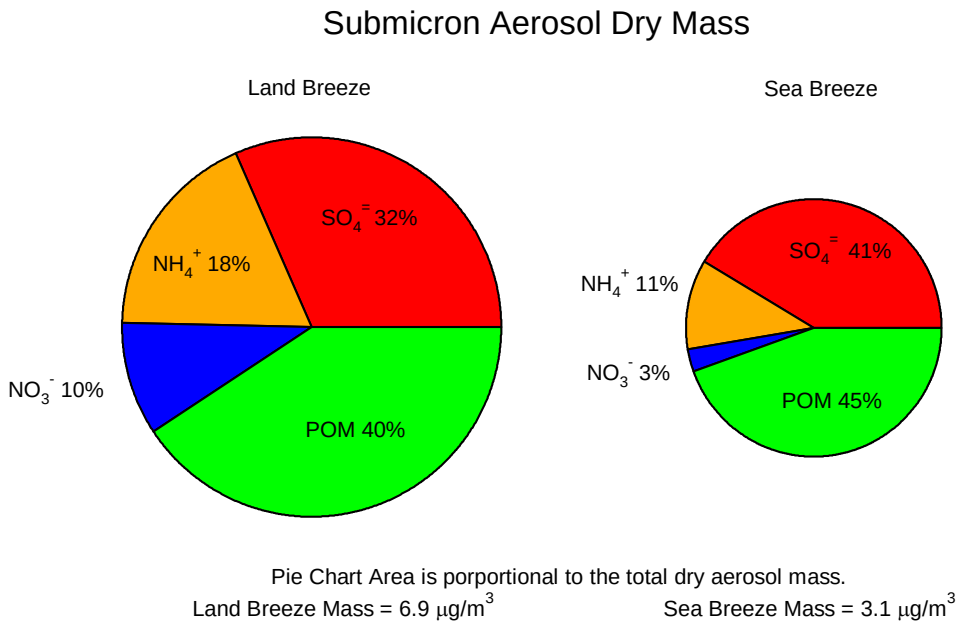




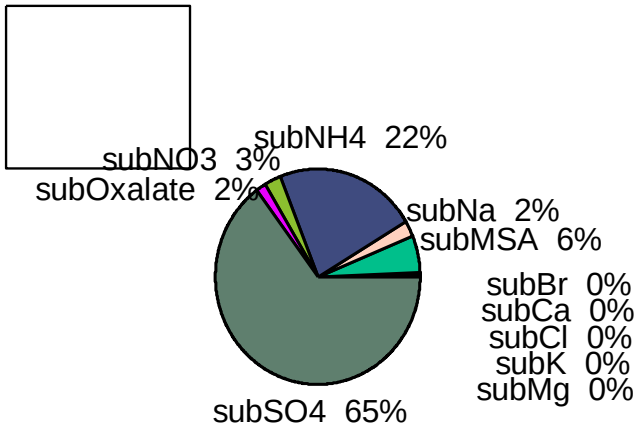
Details of Boxmodeling

	5/16/2011	5/21/2011	5/24/2011	5/25/2011
Distance to the Coast	6.7 km	12.6 km	2.1 km	7.3 km
Transport time	1.8 hours	2.0 hours	0.18 hours	1.1 hours
N_2O_5	23 ± 6 pptv	49 ± 13 pptv	54 ± 19 pptv	8 ± 3 pptv
NO_2	9.4 ± 2.1 ppbv	9.0 ± 0.6 ppbv	14.3 ± 3.2 ppbv	3.2 ± 0.8 ppbv
O_3	35.5± 2.4 ppbv	26.4 ± 3.3 ppbv	21.5 ± 2.6 ppbv	34.8 ± 1.0 ppbv
DMS	35 ± 10 pptv	18 ± 11 pptv	21 ± 10 pptv	15 ± 9 ppbv
$k_{NO3+DMS}$	0.005 s^{-1}	0.0025 s-1	0.0035 s-1	0.0021 s-1
Total Surface Area	960 ± 50 $\mu m^2/cm^3$	1021 ± 50 $\mu m^2/cm^3$	550 ± 50 $\mu m^2/cm^3$	266 ± 20 $\mu m^2/cm^3$
k_{N2O5}	0.0022 s^{-1}	0.0024 s-1	0.0013 s-1	0.00063 s-1
$ClNO_2$ produced over water γ = 100%	**790 pptv**	**720 pptv**	**65 pptv**	**92 pptv**
$ClNO_2$ produced over water	79 pptv ϕ = 10%	360 pptv ϕ = 50%	32 pptv ϕ = 50%	46 pptv ϕ = 50%
$ClNO_2$ Observed	**320 pptv**	**1450 ± 250 pptv**	**580 ± 61 pptv**	**340 ± 41 pptv**

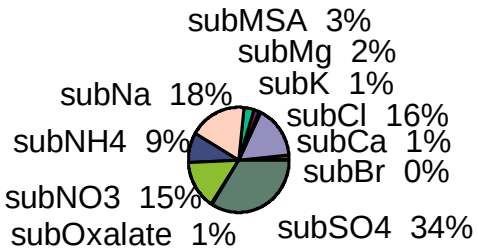
AMS Aerosol Composition: Land Breeze – Sea Breeze



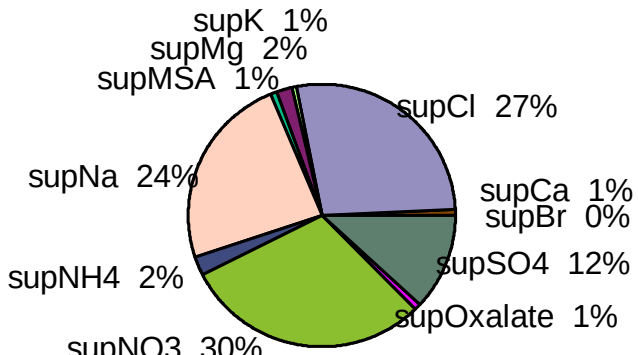
Aerosol Composition – Filter Samples – Land Breeze



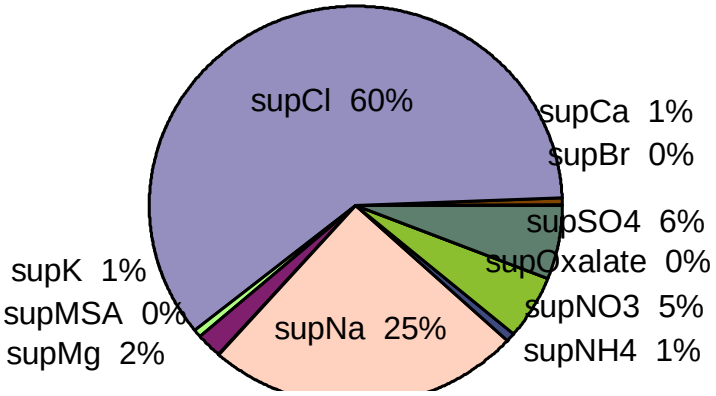
Submicron Land Breeze, filter number 1
5/15 8:19pm - 5/16 7:00 am
mass = 5.6 ug/m3



Submicron Land Breeze, filter number 19
5/23 7:15 pm - 5/24 6:59 am
Mass = 1.3 ug/m3

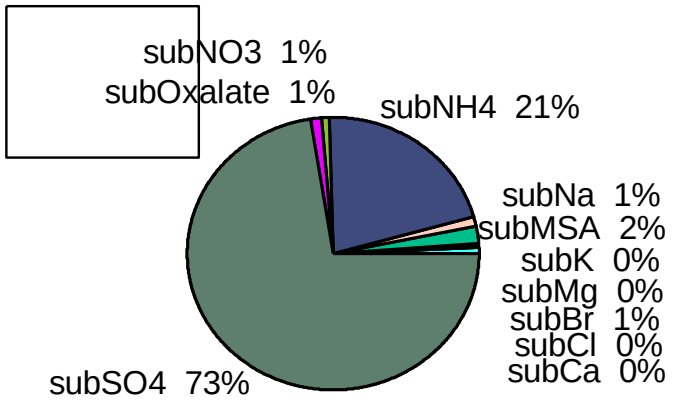


Supermicron Land Breeze, filter number 1
5/15 8:19pm - 5/16 7:00 am
Mass = 9.4 ug/m3

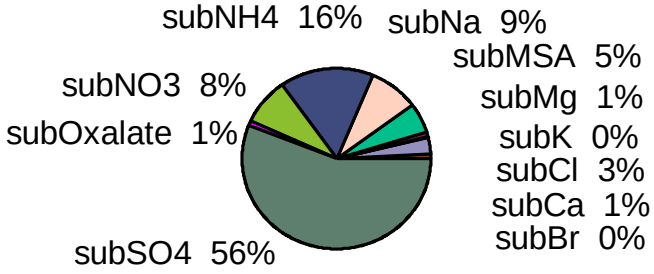


Supermicron Land Breeze, filter number 19
5/23 7:15 pm - 5/24 6:59 am
Mass = 21.7 ug/m3

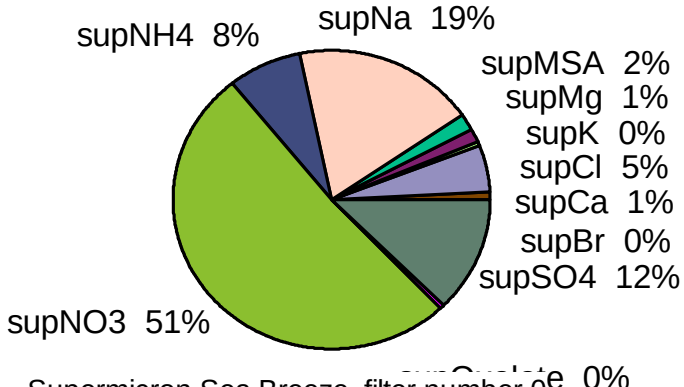
Aerosol Composition – Filter Samples – Sea Breeze



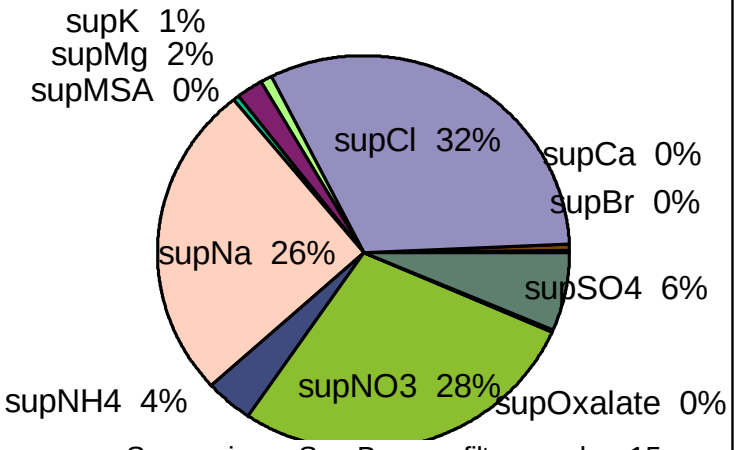
Submicron Sea Breeze, filter number 0
5/15 8:11 am - 5/15 1:34 pm
Mass = 10 ug/m3



Submicron Sea Breeze, filter number 15
5/21 8:40 am - 5/21 12:50 pm
Mass = 4.4 ug/m3



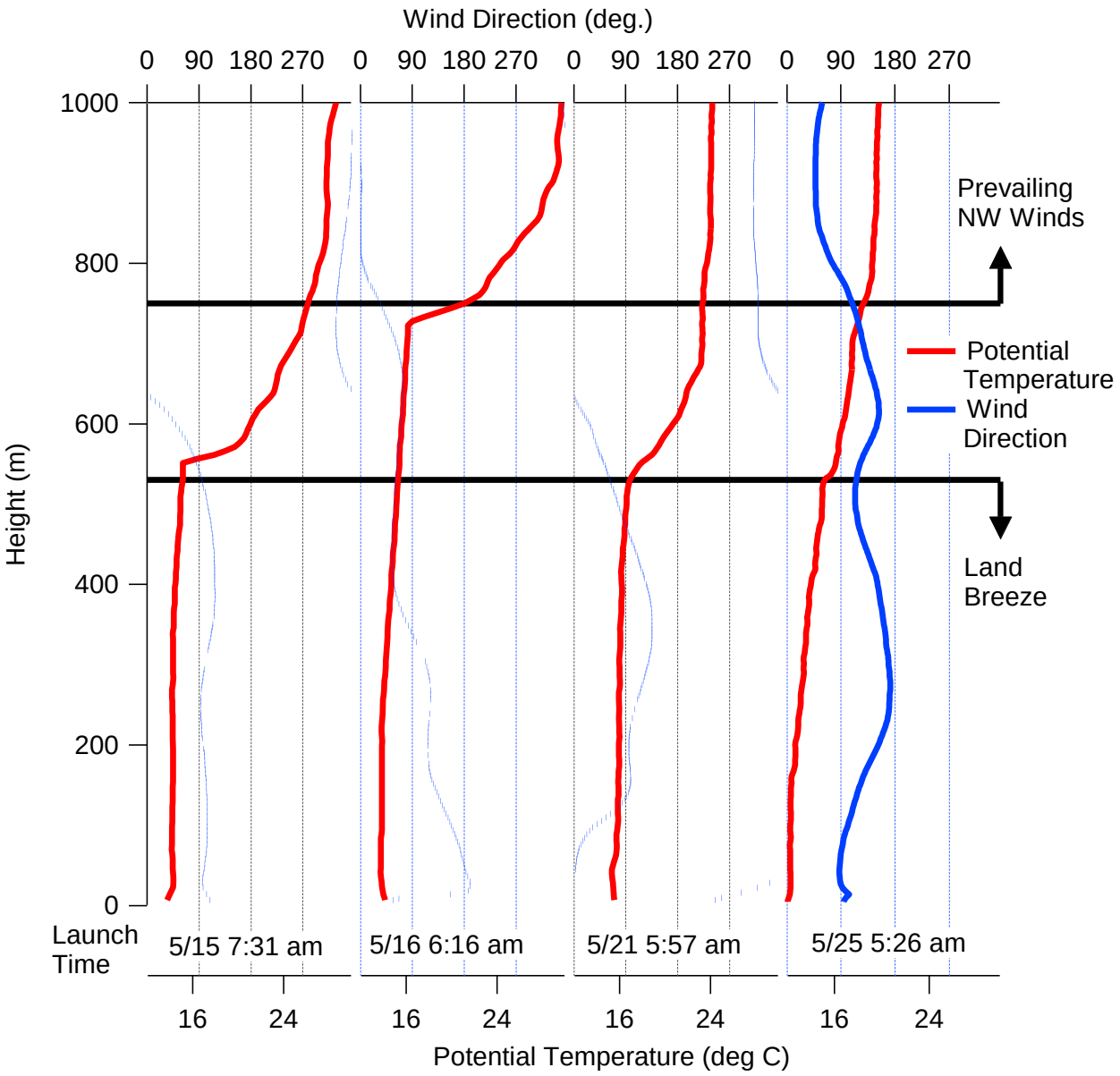
Supermicron Sea Breeze, filter number 0
5/15 8:11 am - 5/15 1:34 pm
Mass = 12 ug/m3



Supermicron Sea Breeze, filter number 15
5/21 8:40 am - 5/21 12:50 pm
Mass = 20.9 ug/m3

Radiosondes Launched from the R/V Atlantis

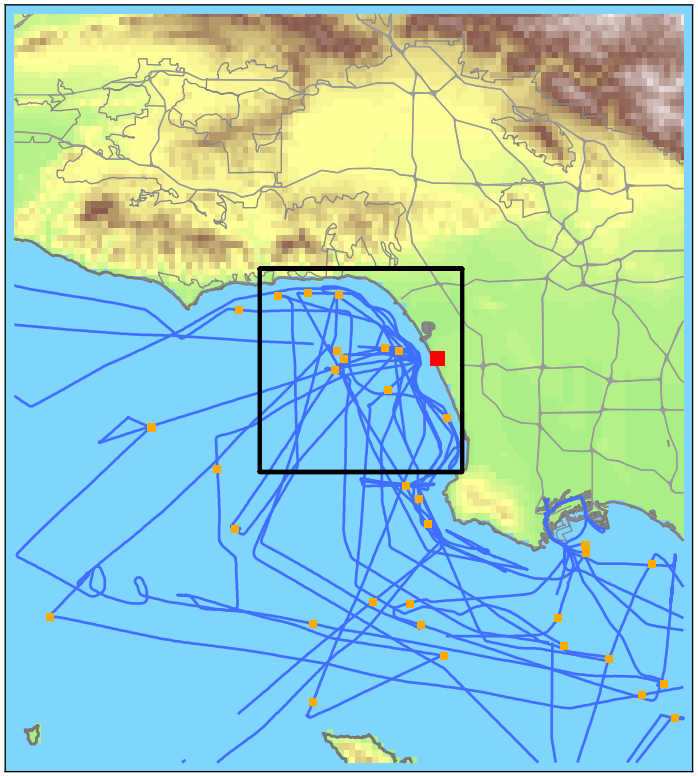
- Four radiosondes launched during the land breeze. (during the night in SMB)
- The marine boundary layer extends up to between 550 and 750 meters.
- Land breeze in the boundary layer from the East - South East.
- Above the marine boundary layer winds are from the northwest.
- R/V Atlantis measurements are representative of the marine boundary layer.



Land Breeze observed on the R/V Atlantis

- The R/V Atlantis observed the land breeze in Santa Monica Bay on five nights. (5/15th, 5/16th, 5/21st, 5/24th and 5/25th)
- The land breeze begins around midnight and continues a few hours after sunrise.

Santa Monica Bay



Diurnal Wind Speed and Direction